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CHEMICAL REACTIONS ON SOLID SURFACES USING MOLECULAR BEAM TECHNI--ETC(U)

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## ABSTRACT

Thermal energy molecular beams have been used to study chemical interactions with metal surfaces. Chemisorption of simple molecules such as  $H_2$ ,  $O_2$ ,  $CH_4$ ,  $C_2H_x$  and CO was investigated on single and polycrystalline surfaces of Pt, Ni, Co, and Ag. Kinetic parameters and reaction mechanisms were determined for model catalytic reactions including CO and  $C_2H_x$  oxidation and methanation from  $H_2$ /CO mixtures. Chemical reactions of  $NO_x$  with CO and  $D_2$  on Pt(111) and other surfaces have been surveyed and the kinetics of NO and  $O_2$  chemisorption have been measured. The theory of adsorption/desorption kinetics is reviewed and certain deficiencies identified.

## 1. INTRODUCTION

This final report summarizes the work performed under ONR Contract No. N00014-72-C-0247 and N00014-77-C-0255 commencing 1 January 1972 and ending 30 September 1980.

Modulated molecular beams have been used to study the adsorption and reaction of chemical species on single crystal metal surfaces. In particular, chemisorption of the simple gases  $O_2$ ,  $H_2$ ,  $CO$ ,  $CH_4$ ,  $C_2H_2$ ,  $C_2H_4$  and  $C_2H_6$  has been investigated on Pt(111) and Ag(111) surfaces. The kinetics of the oxidation of these gases was also studied by the molecular beam technique. Reactions of  $H_2$  with  $CO$  for form hydrocarbon products have also been studied on Ni, Co, and Fe as well as Pt. Surface conditions leading to extraordinarily high activity for the formation of the product  $CH_4$  were found for Ni and Co. Activity enhancements of greater than 10x and 100x, respectively, could be achieved over the clean surface condition by incorporating oxygen into the lattice by exposure to  $O_2$ . These highly active surfaces are stable in  $H_2/CO$  mixtures below 675°K.

## 2. EXPERIMENTAL RESULTS

Molecular beams are widely recognized as the most appropriate technique for studies of chemical interactions on an atomic level. Much of our understanding of the chemical interactions of atoms, molecules, ions and excited species has been achieved by this experimental method. However, relatively little use has been made of beams to study interactions on surfaces. Recent work has demonstrated, however, that beams are extremely useful for these heterogeneous studies as well.

From a physical point of view, molecular beams offer the advantage of allowing the investigator to characterize the initial conditions of the beam species. The incident momentum (angle of incidence), energy, and chemical composition of the beam are readily controlled. Also, the internal energy of the beam species, including rotational, vibrational and electronically excited states can be selected. While we do not currently utilize internal state selection, by simply specifying the incident angle and temperature of a single reactant species on an "ideal" clean, single crystal surface, many of the ambiguities of typical

reaction cell studies are eliminated. First, with beams we can be certain that the products we observe are the result of a single encounter of the beam species with the surface. Modulation of the beam eliminates the contribution of ambient vacuum species or multiple collisions of the beam with other surfaces when phase sensitive detection is employed. Second, after reacting at the surface, line-of-sight mass spectrometry eliminates any subsequent reactions that might change the compositions of the desorbed products. This is of primary importance in catalysis since very reactive chemical radicals can sometimes be generated by surface reactions. Moreover, these initial chemical products are often the intermediates in a series of reactions that occur when multiple surface and gas-phase collisions are allowed. The importance of these subsequent reactions is quickly appreciated if we consider that in a flowing reaction cell, perhaps  $10^{15}$  surface and gas-phase collisions can occur before the chemical composition of the products is determined.

## 2.1 $C_2H_4$ OXIDATION ON Ag(111)

The catalytic oxidation of ethylene ( $C_2H_4$ ) is an important commercial process, ethylene oxide being the thirteenth largest volume organic chemical produced in the U.S. Since Ag is thought to be the catalyst for this process, we undertook a study of the interaction of  $C_2H_4$  with  $O_2$  on Ag(111). The reactivity on Ag(111) was found to be low and below the level of detectability using the conventional molecular beam (M.B.) geometry. Using a modified isotropic source geometry for increased signal the product  $CO_2$  was detected. No  $C_2H_4O$  was detected, however. It was possible with the M.B. configuration to observe the fragmentation of  $C_2H_4$  to  $C_2H_3$  (10%) and  $C_2H_2$  (5%) on Ag(111). The details of this work were presented as Technical Report No. 1 and also published ("Studies of the Catalytic Reaction of  $C_2H_4$  and  $O_2$  on Ag(111) Surfaces" by Joe N. Smith, Jr., R. L. Palmer, and D. A. Vroom, J. Vac. Sci. Technol. 10(2), 373 (1973).

Some investigations of the oxidation of  $C_2H_2$  and CO on Ag(111) were made, but the reactivity was found to be much greater and more amenable to study by M.B. on Pt(111).



## 2.2 CO OXIDATION ON Pt(111)

Pt(111) has a high activity for the oxidation of CO due to its ability to dissociatively chemisorb  $O_2$  without forming an unreactive oxide. The "sticking" coefficient for  $O_2$  on Pt(111) was measured to be about  $10^{-3}$  by titration with CO. The reaction product  $CO_2$  was observed to desorb in a very peaked distribution about the surface normal ( $\sim \cos^6 \theta$ ) indicating an activation barrier to adsorption of  $\sim 7$  kcal/mole. The high mobility of CO on the Pt(111) surface was dramatically demonstrated and indicated primarily a Langmuir-Hinshelwood (L-H) reaction mechanism with the adsorbed CO capable of sampling a large surface area before reacting with a chemisorbed oxygen atom. At temperatures below  $\sim 250^\circ C$  the  $O_2/CO$  balance becomes very critical since CO blocks the chemisorption of  $O_2$ , whereas the oxygen saturated surface still readily chemisorbs CO. Thus, the Pt(111) surface remains catalytically active only for  $O_2/CO \geq \frac{S_{CO}}{S_{O_2}}$  (i.e.,  $\sim 10^2$ ) as the temperature is lowered and/or the total pressure is increased. This figure, of course, would vary for other crystal faces and on rough surfaces because the sticking coefficient of oxygen,  $S_{O_2}$ , is strongly affected by these parameters.

Further details of this work are given in Technical Report No. 2. The results were also published ["Molecular Beam Study of CO Oxidation on a (111) Platinum Surface," R. L. Palmer and Joe N. Smith, Jr., J. Chem. Phys. 60, 1453 (1974)]

## 2.3 $C_2$ HYDROCARBON OXIDATION ON Pt(111)

Further insights into oxidation catalysis on Pt(111) were made in a study of the oxidation of the  $C_2$  hydrocarbons ( $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ). It was found that, aside from the initial sticking probabilities, the oxidation of these three species was identical. This result is consistent with other studies which indicate that the  $C_2$  hydrocarbons chemisorb as an acetylenic species at elevated temperatures. The sticking coefficients for  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$  were  $\sim 1.0$ ,  $\sim 0.5$ , and  $< 10^{-3}$ , respectively. While the chemisorption of  $C_2H_2$  and  $C_2H_4$  were rapid,  $C_2H_6$  chemisorption was quite slow and apparently activated, although the magnitude of its activation barrier was not determined.

The surface temperature dependences of the three oxidation products, CO,  $CO_2$  and  $H_2O$ , were measured and found to have a common slope in excess oxygen of 16 kcal/mole. This result indicates a rate limiting step common to all three products. Since the surface mobility of oxygen is the only process common

to all three products it was concluded that the activation barrier to the diffusion of atomic oxygen is 16 kcal/mole on the Pt(111) surface.

The details of these experiments were written up and circulated as Technical Report No. 3. This work was also published in the open literature ["Molecular Beam Study of Oxygen and C<sub>2</sub> Hydrocarbon Chemisorption and Reactions on Pt(111)," Robert L. Palmer, J. Vac. Sci. and Technol. 12(6), 1403 (1976)].

#### 2.4 H<sub>2</sub>/CO METHANATION STUDIES

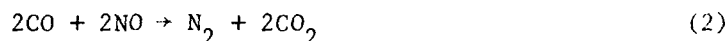
Molecular beams were used to study the important catalytic methanation reaction. After an unsuccessful effort to study the reaction in the 10<sup>-7</sup>-10<sup>-5</sup> torr regime, the apparatus was modified for studies in the 1 torr range. Studies were made on the transition metals in group VIII, but were most extensive on Ni, Co and Fe. Marz grade (99.999%) foil was used in this study at higher pressures, rather than single crystal films. One interesting result of this study was the discovery of greatly enhanced catalytic activity with oxygen treated Ni and Co foils. Enhancements of greater than 10x and 100x, respectively, were seen in the methanation rates on incompletely reduced surfaces. Apparently "doping" of the surface with small amounts of oxygen (1-3%) has a large affect on the catalytic activities of Ni and especially Co. On the other hand, Fe foils showed a decrease in activity after exposure to oxygen. Other workers have also reported increased catalytic activities due to surface oxygen in Rh (Ref. 1), and Pt (Ref. 2). This is an important parameter that has been overlooked in earlier studies on these surfaces, including possibly our own work on Pt(111) which may have been influenced by the presence of small amounts of oxygen.

The mechanism for CH<sub>4</sub> formation on the oxygen activated Ni and Co surfaces was found to involve a surface carbide intermediate, in agreement with the studies by Wise, et al. (Ref. 3) and Ponc (Ref. 4). These results are contrary to the long held belief that the direct dissociation of CO on these surfaces is inconsequential and the important intermediate is either HCO or CHOH. Of course, these intermediates cannot be ruled out for conditions which differ greatly from those which show rapid CO dissociation.

The methanation work has been written up and distributed as Technical Report No. 4, and was published in Journal of Catalysis 50, 244 (1977).

## 2.5 CATALYTIC STUDIES OF NO<sub>x</sub> REACTIONS

Considerable effort was spent examining various catalytic reactions involving N<sub>2</sub>O, NO and NO<sub>2</sub> on single crystal and polycrystalline substrates. The following reactions were attempted on Pt(111) surfaces



Several of these reactions were also attempted on Co and Ni surfaces, but with little success. On Pt(111), reactions (1), (4), and (5) did not proceed at detectable rates. Reaction (2) proceeded at approximately 1/10 the rate of production of CO<sub>2</sub> as with O<sub>2</sub> in place of NO. Reaction (3) was also observed to proceed at detectable rates using either CO or NO<sub>2</sub> in the modulated beam and the other gas over the Pt(111) target. Reaction (6) was investigated using a modulated D<sub>2</sub> beam with NO<sub>2</sub> over the Pt(111) target. At NO<sub>2</sub> pressures above  $\sim 1 \times 10^{-6}$  torr the reaction was poisoned and very little D<sub>2</sub>O was detected. At pressures below  $1 \times 10^{-6}$  torr very dramatic transient behavior was observed with changes in NO<sub>2</sub> pressure. A small increase in NO<sub>2</sub> pressure resulted in a large transient increase in D<sub>2</sub>O, decaying to a steady-state rate in a few seconds. The Pt(111) surface temperature was varied between 650°K and 900°K and the steady state reaction rate increased according to an activation energy of 10 kcal/mole with an NO<sub>2</sub> pressure of  $1 \times 10^{-6}$  torr.

Adsorption isotherms for NO and O<sub>2</sub> were obtained using the attenuation of specular helium scattering as the measure of adsorbate coverage. This technique is described in Technical Report No. 2. Isosteric heats of adsorption of 26 kcal/mole and 21 kcal/mole and pre-exponential or "frequency" factors of  $2 \times 10^7 \text{ sec}^{-1}$  and  $7 \times 10^6 \text{ sec}^{-1}$  were obtained for O<sub>2</sub> and NO adsorption, respectively. These results are somewhat surprising, especially for O<sub>2</sub>, since 26 kcal/mole is a low value for O<sub>2</sub> chemisorption on Pt(111) compared with other published results. Also, the prefactor of  $2 \times 10^7 \text{ sec}^{-1}$  is too high for "normal"

second order desorption and too low for first order desorption. The energy may indicate that we are probing a loosely bound or "precursor" state, although the wide variation in reported heats of adsorption on this and other gas-surface systems may indicate discrepancies of a more fundamental nature so speculations as to the significance of the observed isosteric heat should probably not be taken too seriously. For example, the heat of adsorption of  $H_2$  on Ni has been extensively studied using calorimetric and isosteric methods with results varying from 18-40 kcal/mole. These and other studies of chemisorption also exhibit "compensation" between the kinetic prefactor and the energy; i.e., larger heats of adsorption tend to have larger prefactors associated with them. This so-called "compensation effect" is observed in a wide variety of activated phenomena and is discussed in Technical Report No. 7.

## 2.6 ADSORPTION/DESORPTION KINETICS

Our understanding of chemical reaction mechanisms is based largely on the interpretation of kinetic data so that a possible fundamental relationship between the prefactor and energy in kinetic studies is of obvious importance. Accordingly, we have considered various theories of prefactors in order to determine if there exists a basis for the compensation effect. One derivation of the adsorption isotherm, obtained first by Langmuir and later by Fowler and Eyring, is

$$p = \frac{kT(2\pi mkT)^{3/2}}{N_s h^3} \frac{f_g}{f_a} \exp - \frac{e_a}{RT} \quad (7)$$

where the  $f$ 's are the adsorbate and gas partition functions and  $e_a$  is the activation energy of desorption. The rate of desorption can be obtained from this expression by noting that if we divide the left side by the factor  $(2\pi mkT)^{1/2}$  we have the rate of impingement from the gas phase which must equal the rate of desorption at equilibrium (assuming unit sticking probability). Thus

$$\frac{p}{(2\pi mkT)^{1/2}} = \frac{2\pi mkT}{N_s h^3} \frac{f_g}{f_a} \exp - \frac{e_a}{RT} \quad (8)$$

The derivation of (7) is based on equating the chemical potentials of the gas and adsorbed phases and not on the kinetics of the process. In fact, Fowler explicitly states that "The isotherm (7) must hold whatever the kinetics of the

process, provided only that the molecules are adsorbed onto definite sites and do not interact with one another" (Ref. 5). In fact, this statement is in error inasmuch as (7) is only valid for a first order process as we shall show below. Another approach to an a priori calculation of the prefactor is to consider a particle in a box and calculate the frequency of wall collisions with energy greater than a specific activation  $\epsilon^*$ . For this case Fowler gives

$$r^* = \frac{3}{2a} \left( \frac{2kT}{\pi m} \right)^{1/2} \exp - \frac{\epsilon^*}{RT} \quad (9)$$

where  $a$  is the dimension of the cubical box. If we assume only 1/6 of the collisions are normal to the external surface and can evaporate, then.

$$r_d^* = \frac{1}{4a} \left( \frac{2kT}{\pi m} \right)^{1/2} \exp - \frac{\epsilon^*}{RT} \quad (10)$$

A desorption rate can also be derived from basic thermodynamics starting with the volume concentrations in the gas and adsorbed phases  $|G|$  and  $|A|$ , respectively. Then

$$\left| \frac{G}{A} \right| = \exp \frac{\Delta S}{R} \exp - \frac{\Delta H}{RT} \quad (11)$$

and  $|G| = p/kT$  and  $|A| = \frac{1}{a} \left( \frac{\theta}{1-\theta} \right)$  where  $a$  = thickness of adlayer. (11) then becomes

$$p = \frac{kT}{a} \left( \frac{\theta}{1-\theta} \right) \exp \frac{\Delta S}{R} \exp - \frac{\Delta H}{RT} \quad (12)$$

Since  $\exp \frac{\Delta S}{R}$  is just the ratio of the partition functions of the gas and adsorbed state, in this respect (12) is similar to (7), but there are other obviously different terms in the prefactor. Again, we can divide both sides of (12) by  $(2\pi mkT)^{1/2}$  to get a rate expression which gives

$$\frac{p}{(2\pi mkT)^{1/2}} = \frac{1}{a} \left( \frac{kT}{2\pi m} \right)^{1/2} \left( \frac{\theta}{1-\theta} \right) \exp \frac{\Delta S}{R} \exp - \frac{\Delta H}{RT} \quad (13)$$

To compare these results, for example, for CO at 300°K from Eq. (8)

$$\frac{2\pi mk T^2}{N_s h^3} \approx 1.7 \times 10^{15}$$

from Eq. (10),  $\frac{1}{4a} \left( \frac{2kT}{\pi m} \right)^{1/2} = 6 \times 10^{11}$  for  $a = 10^{-8}$  cm and from Eq. (13),  $\frac{1}{a} \left( \frac{kT}{2\pi m} \right)^{1/2} = 1.2 \times 10^{12}$  for  $a = 10^{-8}$  cm.

The lack of a  $\theta$  dependence in (10) is the result of considering only a single particle in a box. More significantly the absence of the  $\exp \frac{\Delta s}{R}$  or  $f_g/f_a$  factor in (10) reflects an inherent flaw in the model. The derivation of (13) achieves the  $\exp \frac{\Delta s}{R}$  dependence in the rate without benefit of any model for the desorption process, but the rest of the prefactor differs significantly from (8) so that one of these results must be assumed to be in error. A derivation equivalent to (8) has been expanded by Ibach, et al. to include additional internal states. We are not aware of previous derivations of the desorption rate (13) although the assumptions are few and the thermodynamic basis is fundamental.

Transition state theory has also been used to derive desorption kinetics. The rate is usually expressed as,

$$r_d = \frac{kT}{h} \frac{\theta}{1-\theta} \frac{f^\ddagger}{f_a} \exp - \frac{\epsilon_a}{RT} \quad (14)$$

where  $f^\ddagger$  is the partition function of the transition state and  $\epsilon_a$  is the adsorption energy. Transition state theory is the only derivation that obtains a kinetic dependence of the rate on the partition functions explicitly from a feature of the model. Specifically, the rate of transitions across the reaction surface is assumed to be proportional to the area of that surface in phase space; that is, the rate is governed by the ratio of points in phase space on the reaction surface to the total phase space volume of the reactant. While this simplified model provides a basis for calculation of many chemical rates, not just evaporation, we have raised the question as to whether transition state theory is consistent with basic thermodynamic boundary conditions. This question arises when comparing (14) with either (8) or (13) since  $f^\ddagger/f$  is not, in general, equal to  $f_g/f_a$  or  $\exp \frac{\Delta s}{R}$ . As far as the rest of the prefactor in (14),  $kT/h = 6.25 \times 10^{12}$  at 300°F, for comparison with (8), (10), and (13).

One would hope to be able to determine the correctness of the above or other kinetic rate expressions by appealing to careful measurements of desorption rates. Unfortunately, the rate is dominated by the energy terms to the extent that the temperature dependence of the prefactor cannot be easily determined. However, this subtle difficulty is overshadowed by the fact that experimentally determined values of prefactors are observed to vary by many orders of magnitude, both within a given series of measurements and from laboratory to laboratory. Large differences in prefactor values can easily be attributed to changes in the ratio of the partition functions of the adsorbed and/or transition or gas phase. This ratio or its equivalent, the  $\exp \frac{\Delta S}{R}$  term can exceed  $10^6$  for an immobile adlayer versus an ideal gas. These problems can be eliminated experimentally by making measurements at the critical point where  $\Delta H$  and  $\Delta S = 0$ . Prefactors calculated from data in the literature for species at their critical points are the following:

$v_{H_2O} = 5 \times 10^{10}$ ,  $v_{CO_2} = 1.7 \times 10^{10}$ , and  $v_{H_2} = 4.2 \times 10^{10}$ . These results are too limited to be persuasive, but a worthwhile approach to determining the proper kinetic expression may be to compare careful measurements of the critical points of various species of widely differing masses since each of the derivations arrives at very different dependences on mass. In Table 1, data are given for the critical temperatures and pressures for the four species mentioned above and calculated critical pressures based on Eqs. (12) and (14). Equation (12) contains the adjustable parameter  $a$ , the adlayer thickness which was chosen to be  $50\text{\AA}$  in order to give good agreement with the experimental values. Equation (14) has no adjustable parameters and the critical pressures calculated from (14) are over two orders of magnitude high for every species except  $H_2$ . The error in absolute values for Eq. (14) is less serious than the apparently wrong mass dependence since Eq. (12) gives about the same degree of accuracy for all of the species from mass 2 amu to mass 44 amu. Again, these results are too sparse to be a compelling test of these or other kinetic models, but the results are certainly suggestive and perhaps further efforts in this direction would clarify the question of the proper kinetic expression.

So far, the issue of the sticking coefficient or its analogue, the transmission factor, has been neglected in the above discussion of kinetic rates.

TABLE 1

Species	$T_c$ (°K)	$P_c$ (atm)	$p(\text{calc})^*$	$p'(\text{calc})^{**}$
$C_2H_6$	305	48.8	82	22,700
$CO_2$	304	73	82	27,200
$H_2O$	647	217.72	175	54,300
$H_2$	33	12.8	9.0	209

$$^* \text{ where } p(\text{calc}) = \frac{10^{15} k T_c}{1.336 \times 10^3 a} \quad (\text{where } a = 50 \times 10^{-8} \text{ cm})$$

$$^{**} p'(\text{calc}) = \frac{10^{15} k T_c (2 \pi m k T_c)^{1/2}}{1.336 \times 10^3 h}$$



In the expressions for equilibrium pressure, such as Eqs. (7) and (12), sticking coefficients or transmission factors have no affect. However, in rate expressions such as (8), (13), and (14), this kind of term should be included. If we want to obtain the kinetics, say of desorption, by measuring a rate, then we must also measure the sticking coefficient versus coverage and temperature,  $S(\theta, T)$ . This can be related then to a desorption function  $D(\theta, T)$  where

$$\frac{S(\theta, T)}{D(\theta, T)} = (1-\theta)^n \quad (15)$$

and  $n$  is the idealized order of the desorption kinetics; i.e.,  $n = 1, 2$ , etc. With this modification then Eq. (13) becomes

$$\frac{p S(\theta, T)}{(2\pi mkT)^{1/2}} = \frac{1}{a} \left( \frac{kT}{2\pi m} \right)^{1/2} \theta^n D(\theta, T) \exp \frac{\Delta S}{R} \exp - \frac{\Delta H}{RT} \quad (16)$$

Thus, in the limit of  $D(\theta, T) = 1$  we have "Langmuir" adsorption and, with  $S(\theta, T) = 1$  we have "precursor" adsorption kinetics. Experimentally,  $S$  and  $D$  usually fall somewhere between these two limits, so that  $S(\theta, T)$  needs to be measured explicitly.

We have, thus far, also not discussed the coverage dependence of the kinetics. This subject has been thoroughly addressed elsewhere, but some comments are in order as it pertains to the results obtained above. First, Eqs. (7), and (12) both agree in having a  $\left(\frac{\theta}{1-\theta}\right)$  dependence on coverage. Since this term goes to infinity at full coverage this is obviously an unrealistic condition. The  $(1-\theta)^{-1}$  part of this term is most easily understood from the derivation of (12) based on the ratio of molecular volume concentrations of the gas and adsorbed states. In this derivation  $\left(\frac{\theta}{1-\theta}\right)$  represents the volume concentration of the condensed phase. But this is an idealization based on filling a fixed adsorbed state volume to capacity with no left over volume at  $\theta = 1$ . For example, filling a box with small cubes that fit the available space ideally. Kisliuk has proposed a dependence of the form  $\left(\frac{\theta^{\alpha}}{1-\theta^{\alpha}}\right)$  where  $\alpha \leq 1$  (Ref. 8). This can be visualized as filling a box with ill-fitting particles, which leaves some volume left unfilled at maximum packing. The value of  $\alpha$  must, of course, be determined experimentally for each case of interest by measuring  $S(\theta, T)$  to obtain  $D(\theta, T)$  where, in this case,

$$\frac{S(0,T)}{D(0,T)} = (1-\alpha\theta)^n$$

### 3. SUMMARY

One conclusion to be reached from the above discussion is that the kinetics of even the simplest chemical process is poorly understood. Careful experimental investigation of chemical rates for simple processes such as desorption or adsorption should contribute significantly to identifying the proper kinetics for these and other more complicated chemical paths. Molecular beam studies of adsorption and desorption will undoubtedly contribute much more to clarifying this problem. Previous studies in this program have shown that adsorption is often energy dependent and that, conversely, desorption is also frequently non-Boltzmann. This demonstrates that adsorption/desorption phenomena cannot be treated kinetically using the usual assumption of an isothermal reaction path. These results also raise a question as to the validity of the isothermal assumption for the more general class of chemical reactions. For reaction steps involving large changes in the number of degrees of freedom or entropy of the system, large changes in the local temperature along the reaction path is possible if the thermal coupling with the surrounding system is weak. For example, heat is released during the adsorption of a gas at finite temperatures on a surface, even if the heat of adsorption is zero because of the loss of those degrees of freedom that contain finite energy. The kinetics of the relaxation of these energy modes, rotation and vibration for example, may play an important role in the kinetics of these processes. Studies of adsorption and desorption also provide a unique opportunity to test transition state theory under a range of experimental conditions such as coverage and temperature. As was mentioned above, the kinetics of transition state theory as applied to desorption appear to be in conflict with the thermodynamic requirements of this process. Measurements of energies and prefactors for desorption show widely varying results that much more often than not exhibit so-called compensation. If the transition state partition function really does determine the kinetics of reactions then this compensation effect may be the mechanism by which the apparent discrepancy in overall rates, as for example, between Eqs. (13) and (14) is resolved.

#### 4. PUBLICATIONS AND PRESENTATIONS

##### 4.1 PAPERS PUBLISHED

1. "Studies of the Catalytic Reaction of  $C_2H_4$  and  $O_2$  on Ag(111) Surfaces," Joe N. Smith, Jr., R. L. Palmer, and D. A. Vroom, J. Vac. Sci. and Technol. 10(2), 373 (1973) (Technical Report No. 1).
2. "Molecular Beams Study of CO Oxidation on a Platinum Surface," R. L. Palmer and Joe N. Smith, Jr., J. Chem. Phys. 60, 1453 (1974) (Technical Report No. 2).
3. "Molecular-Beam Study of Oxygen and  $C_2$  Hydrocarbon Chemisorption and Reactions on Pt(111)," Robert L. Palmer, J. Vac. Sci. and Technol. 12(6), 1403 (1975) (Technical Report No. 3).
4. "Mass-Spectrometric Measurements of Enhanced Methanation Activity Over Cobalt and Nickel Foils," R. L. Palmer and D. A. Vroom, J. Catal. 50, 244 (1977).
5. "Study Surfaces with Molecular Beams - Catalytic and Otherwise," CHEMTECH (1978), p. 702.
6. "Low Energy Electron Diffraction Study of the Surface Defect Structure of Ag(111) Epitaxially Grown on Mica," (with D. G. Welkie and M. G. Lagally), J. Vac. Sci. Tech. 17, 453 (1980).
7. Comments on "An Example of 'Fast' Desorption Anomalously High Pre-Exponentials for CO Desorption from Ru(001)," submitted to Chem. Phys. Letters.

##### 4.2 TALKS PRESENTED

1. "Studies of the Catalytic Reaction of  $C_2H_4$  and  $O_2$  on Ag(111) Surfaces," Joe N. Smith, Jr., R. L. Palmer, and D. A. Vroom, American Vacuum Society Meeting, Chicago, Ill., Oct. 1972
2. "Molecular Beam Studies of Oxidation on (111) Pt Surfaces," R. L. Palmer and Joe N. Smith, Jr., Third North American Meeting of the Catalysis Society, San Francisco, Feb. 1974.
3. "Molecular Beam Studies of Catalytic Oxidation on Pt Surfaces," R. L. Palmer and Joe N. Smith, Jr., Third North American Meeting of the Catalysis Society, San Francisco, Feb. 1974.
4. "Oxidation of the  $C_2$  Hydrocarbons on Pt(111) Films," R. L. Palmer, California Catalysis Society, Anaheim, November 1974.

5. "Studies of H<sub>2</sub>/CO Reactions Using a Fast Flow Catalytic Reactor," R. L. Palmer, California Catalysis Society, Berkeley, March 1976.
6. "Studies of CO and Hydrogen Reactions on Cobalt and Nickel Surfaces at Low to Intermediate Pressures," R. L. Palmer, Gordon Research Conference on Catalysis, New London, June 1976.
7. "Molecular Beam Studies of Model Catalytic Chemical Reactions," R. L. Palmer, American Chemical Society, New Orleans, March 1977.
8. "Entropy Factor in Adsorption-Desorption Kinetics," Symposium on Non-Equilibrium States in Chemical Reaction Engineers, American Institute of Chemical Engineers Meeting, San Francisco, November 1979.
9. "Molecular Beam Studies of Non-Random Phase Transitions," Gordon Research Conference on Catalysis, New London, 1980

#### REFERENCES

1. B. A. Sexton and G. A. Somorjai, J. Catal. 46, 167 (1977).
2. R. W. McCable and L. D. Schmidt, Surface Sci. 60, 85 (1976).
3. P. R. Wentrecek, B. J. Wood, H. Wise, J. Catal. 43, 363 (1976).
4. J. J. Stephan and V. Ponec, J. Catal. 44, 439 (1976); W. L. van Dijk, J. A. Groenewegen, V. Ponec, 45, 277 (1976).
5. R. Fowler and F. A. Guggenheim, Statistical Thermodynamics, Cambridge (1956), p. 247.
6. Ibid p. 533.
7. H. Ibach, W. Erley and H. Wagner, Surface Sci. 92, 29 (1980).
8. P. J. Kisliuk, J. Phys. Chem. Solids 3, 95 (1957); 5, 5 (1958).

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